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SUBJECT: ANALYSIS OF THE HISTORICAL AND REVISED BASE YEAR 1990
            VOLATILE ORGANIC COMPOUND EMISSION INVENTORIES

BACKGROUND

The Department of Pesticide Regulation (DPR), the Air Resources Board (ARB), and ARB's Agricultural Advisory Committee for Air Quality, Emission Inventory Subcommittee met on November 7, 2002, in Modesto to discuss Volatile Organic Compound Emission (VOC) issues. The advisory group is comprised largely of ARB's agricultural stakeholders. One topic of discussion during the meeting was DPR's recently revised pesticide VOC inventory calculation procedures (Spurlock, 2002b), and particularly the effect of revision on base year 1990 emission estimates. Members of the subcommittee expressed concern that the prior, or historical emission inventory, showed 1990 emissions were greatest in the decade 1990 - 1999, whereas the revised inventory calculations yielded 1990 emissions that were lower than several other years (Figure 1). This is unusual due to the relatively low reported pesticide use in 1990 (Figure 2). The magnitude of 1990 emissions relative to other years is important because VOC emission reduction goals are expressed as a fraction of base year (1990) emissions. Consequently, reduction goals are more difficult to meet if base year emissions are low relative to future years.

The potential VOC emission from a given application of a pesticide product is:

$$\text{emission (pounds)} = \text{(pounds product applied)} \times \text{(product emission potential)}$$

Annual emissions are calculated as the sum of emissions from all individual pesticide applications. Consequently, it's expected that annual VOC emissions be approximately correlated with annual pesticide use. While the expected relationship is apparent in the revised data, there is no significant correlation between historical emission data and use (Figure 3). Figure 3 also illustrates the previous point: disproportionately high base year 1990 emissions relative to pesticide use.

This memorandum addresses two specific questions:
1. Why are historical inventory base year 1990 VOC emissions high relative to 1990
    pesticide use as compared to all other years?
2. Are the historical emission inventory data generally reliable?

DISCUSSION

determining EPs   In the mid-1990s DPR requested that pesticide registrants submit
thermogravimetric analytical (TGA) data for all products that were then registered for
agricultural or commercial structural uses (e.g., DPR, 1995). The TGA data are used to
determine product emission potentials (EP). The data call-in was voluntary, and registrants
submitted TGA data for only a fraction of then-registered products. DPR developed several
alternate methods to estimate product EPs for those products without TGA data. These methods
included water subtraction, inorganic subtraction, and the assignment of default EPs. The
"subtraction" methods assumed that all product components except water or inorganic materials
contributed to VOC emissions, whereas the default method involved defining constant EPs based
on formulation category (e.g., emulsifiable concentrate, flowable concentrate, dusts and
powders).

maximum- and median-value default EPs   Default EPs were defined in the historic inventory
as the maximum TGA-based EP for any product in a particular formulation category. For
instance, the 46 TGA-based EPs for the formulation "flowable concentrate" range in value from
0 to 95.8 percent, with a median of 4.8 (Figure 4). Consequently, the historical maximum-value
default EP assigned to those flowable concentrate pesticides without TGA data was 95.8.
Obviously maximum-value default EPs are many times greater than nearly all measured TGA
values in a formulation category. The net effect of maximum-value default EPs is to bias
calculated VOC product emissions upward. The magnitude of bias in any particular year was
dependent on the proportion of maximum-value default EP product use; in years with greater use
of such products the inventory displayed a greater upward bias.

The revised inventory calculations utilize default EPs defined as the median of TGA-based EPs
in each formulation category (Spurlock, 2002a). In the example above, the revised default EP
for flowable concentrates is 4.8 (Figure 4). The change to median-value default EPs "stabilized"
the inventory by sharply reducing year-to-year fluctuations in emissions due to higher or lower
use of default EP products. This change also yielded a more realistic emission inventory.
Historical and revised default EPs for each formulation category are given in Table 1.

the historical 1990 base year inventory   The TGA data call-in did not apply to older
products that were no longer registered; default EPs were assigned to many of these products.
The fraction of applied products without TGA data was greatest in the early years of the VOC
inventory; in 1990 the fraction of "maximum-value default EP" products applied was greater

than in any subsequent year (Figure 5). Similarly, the greatest fraction of total annual emissions attributable to maximum-value default EP products was also in 1990 (Figure 6). In summary, inflation of the historical base year 1990 emissions was much greater than in any other years.

TABLE 1. Historical and revised default EPs for various formulation classes.

Formulation Code	Formulation	historical maximum TGA default EP	revised median TGA default EP
A0	DUST/POWDER	59.7	1.53
B0	EMULSIFIABLE CONCENTRATE	98.7	39.15
C0	FLOWABLE CONCENTRATE	95.8	4.80
E0	GRANULAR/FLAKE	20.3	3.70
H0	OIL	3.9	3.47
J0	PELLET/TABLET/CAKE/BRIQUET	8.2	5.18
L0	PRESSURIZED GAS	100[†]	100[†]
M0	PRESSURIZED LIQUID/SPRAYS/FOGGERS	100[†]	100[†]
N0	SOLUBLE POWDER	5.3	1.15
O0	SOLUTION/LIQUID (READY-TO-USE	99.9	7.30
P0	WETTABLE POWDER	9.2	1.85
Q0	AQUEOUS SUSPENSION	9.4	see S0 below
R0	DRY FLOWABLE	5.8	1.02
S0[‡]	LIQUID CONCENTRATE	97.3	5.71

† default EP of all pressurized products defined as 100.

‡ Q0 and S0 formulation classes combined in revised inventory due to (a) low number of Q0 products (n=6) and (b) no significant difference in median TGA for these formulation classes (Wilcoxon rank sum test, p = 0.8) (Spurlock, 2002a).

default EPs and specific pesticide families   This section discusses the historical 1990 inventory emission estimates for the top 10 contributing active ingredients (Table 2).

Table 2. Historical and revised 1990 base year emissions for top 10 contributing active ingredients in historical inventory [†]

Dominant active ingredient	1990 lbs products applied	Fraction total historical emissions	Historical 1990 emissions pounds ROG	Revised 1990 emissions pounds ROG
METHYL BROMIDE	4760227	0.13	4758213	5036375
SODIUM CHLORATE	15717099	0.12	4281796	0
1,3-DICHLOROPROPENE	3261446	0.09	3258190	3294425
CHLORPYRIFOS	2618482	0.07	2372879	946508
PETROLEUM OIL,unclassified	11026659	0.06	2291210	165269
METAM-SODIUM	12901193	0.05	1694020	2407552
TRIFLURALIN	3742751	0.04	1489006	403953
ORYZALIN	1006137	0.03	1002353	73194
DIMETHOATE	1587655	0.02	852686	472388
SULFUR	40664827	0.02	802798	227681

[†] emissions for a "dominant active ingredient" defined as sum of emissions for all products in which the listed active ingredient is present as the active ingredient at the highest percentage.

1. methyl bromide

The use of alternate default EPs is not an issue for methyl bromide products because all products containing methyl bromide are assigned EPs of essentially 100% in both the historical and revised inventories. Methyl bromide emissions are essentially equal to product use (EP ~ 100%). Use of methyl bromide increased from 1990 through 1992, then stayed at relatively high levels until the late 90s (Figure 7).

- methyl bromide emissions do not contribute to the disproportionately high 1990 historical inventory in NAA 2 as compared to later years.

2. sodium chlorate

The highest sodium chlorate historical emissions occurred in 1990, even though use of sodium chlorate products was greater in several future years (Figure 8a). The mean sodium chlorate product EP in 1990 – defined as *(total annual sodium chlorate emissions)/(total annual use)* – was highest in 1990, and declined steadily in future years (Figure 8b). Emission potentials of virtually all sodium chlorate products applied in 1990 were determined by inorganic subtraction (Figure 7c), and many of these EPs exceeded 50%. In contrast, EPs determined from TGA data were near or equal to zero. While the relative use of "high EP" inorganic subtraction sodium chlorate products declined through the 1990's, their contribution to total sodium chlorate emissions remained close to 100% (Figure 8c). This is a direct result of sodium chlorate

inorganic subtraction EPs being unrealistically high. In the revised inventory sodium chlorate products are assigned an EP of zero based on an evaluation of sodium chlorate product compositions and fundamental chemical principles (Spurlock, 2002a).

- Sodium chlorate product emissions were disproportionately high in 1990 relative to use because a large proportion of 1990 applied sodium chlorate products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.
- The historical inventory is flawed in that sodium chlorate products are responsible for a significant portion of VOC emissions even though these products are primarily inorganic and nonvolatile (Spurlock, 2002a). Sodium chlorate products are now assigned EPs close to or equal to zero.

3. 1,3 - dichloropropene

The use of default EPs is not an issue for 1,3 - dichloropropene products because all products containing 1,3 - dichloropropene are assigned EPs of essentially 100% in both the historical and revised inventories. Emission of 1,3 – dichloropropene are essentially equal to use (EP ~ 100%). Use of 1,3 - dichloropropene dropped to almost zero in 1991 from high levels in 1990, but the increase in methyl bromide use was nearly commensurate with the decrease in 1,3 – dichloropropene (Figure 7). The decrease in 1,3-dichloropropene use also affected the revised inventory in a similar manner as the historical inventory, but the revised inventory does not demonstrate high 1990 emissions.

- The decrease in 1,3 - dichloropropene use is insufficient to explain the disproportionately high 1990 historical inventory emissions in NAA 2 because the decline in 1,3 – dichloropropene use was offset by increased use of the substitute fumigant methyl bromide.

4. chlorpyrifos

Historical chlorpyrifos product emissions in 1990 exceeded those in 1993, 1998, and 1999 even though total product use was greater in those years (Figure 9a). Lower estimated emissions were observed in later years due to the steady decrease in annual mean chlorpyrifos product EPs throughout the 90s (Figure 9b). This EP decrease was, in turn, due to the steady decline in applied maximum-value default EP chlorpyrifos products (Figure 9c).

- Chlorpyrifos product emissions were disproportionately high in 1990 relative to use because a large proportion of applied chlorpyrifos products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.

5. petroleum oil, unclassified

Historical petroleum oil (unclassified) product emissions in 1990 exceeded those in future years even though total product use was greater in later years (Figure 10a). Lower estimated emissions were observed in later years due to the decrease in annual mean petroleum oil (unclassified) product EPs throughout the 90s (Figure 10b). This EP decrease was, in turn, due to the steady decline in applied maximum-value default EP petroleum oil unclassified products (Figure 10c).

- Petroleum oil, (unclassified) product emissions were disproportionately high in 1990 relative to use because a large proportion of applied petroleum oil (unclassified) products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.

6. metam sodium

While calculated historical metam sodium product emissions were somewhat greater in 1990 than 1991 (by ~ 1.5 million pounds), emissions increased markedly during the latter part of the decade (Figure 11a). Metam sodium products are fumigants that evolve the organic compound active ingredient methyl isothiocyanate (vapor pressure 16 torr at 25C). In the historic inventory, metam sodium products with TGA-based EPs contribute NO emissions even though these products account for up to 75% of metam sodium product use in some years (Figure 11b). This occurred because metam sodium product EPs determined from TGA data equaled zero; the TGA test procedure was inappropriate for metam sodium products (Spurlock, 2002a).

- Based on the emissions of metam sodium products in 1990 – 1999, there was little, if any, contribution of metam sodium emissions to the disproportionately high NAA 2 emissions observed in 1990.
- The historical procedure that led to EP=0 for metam sodium TGA products is unrealistic and is a major flaw in the historical inventory.

7. trifluralin

Throughout the decade historical trifluralin emissions steadily decreased from their maximum in 1990 in spite of large fluctuations in trifluralin product use (Figure 12a). The reason for decreased emissions was the steady decrease in annual mean trifluralin product EPs (Figure 12b). This decrease in mean EP was, in turn, due to the steady decline in applied maximum-value default EP trifluralin products (Figure 12c).

- Trifluralin product emissions were disproportionately high in 1990 relative to use because a large proportion of applied trifluralin products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.

8. oryzalin

Historical oryzalin product emissions declined steadily throughout the 90s from the relatively high levels observed in 1990 – 1992 (Figure 13a). The decrease was due to a decline in annual mean oryzalin product EPs (Figure 13b) attributable, in turn, to the steady decline of applied maximum-value default EP oryzalin products (Figure 13c).

- Oryzalin product emissions were disproportionately high in 1990 relative to use because a large proportion of applied oryzalin products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.

9. dimethoate

Historical dimethoate product emissions were greatest in 1990 (Figure 14a). Annual mean dimethoate product EPs (Figure 14b) declined throughout the 90s attributable, in turn, to the steady decline of applied maximum-value default EP dimethoate products (Figure 14c).

- Dimethoate product emissions were disproportionately high in 1990 relative to use because a large proportion of applied dimethoate products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.

10. sulfur

Historical sulfur product emissions declined through the 90s even though total sulfur product use generally increased during the decade (Figure 15a). The decrease was largely due to a decline in annual mean sulfur product EPs (Figure 15b) attributable, in turn, to the general decline of applied "maximum-value default EP" sulfur products (Figure 15c). The large contribution of "maximum-value default EP" sulfur products to total emissions is particularly striking, and emphasizes the unrealistic results that can be obtained from maximum value default EPs.

- Sulfur product emissions were disproportionately high in 1990 relative to use because a large proportion of applied sulfur products in 1990 were default EP products. The EPs for these products were much higher than those determined by other methods such as TGA.

CONCLUSION

The questions that this memorandum addresses are:

**1. Why are historical inventory base year 1990 VOC emissions high relative to 1990
    pesticide use as compared to all other years?**
Answer: The historical pesticide VOC emission inventory shows extremely high 1990 base year
emissions due to the high use of products with default EPs as compared to other years. These
default EPs were defined as the maximum TGA-based EP in each formulation category. While
the maximum-value defaults cause upward bias in all years of the historical inventory, the effect
is particularly severe for early inventory years – and especially the base year 1990 - when the
fraction of applied products with maximum-value default EPs was greatest. The bias effect of
maximum-value defaults on 1990 emissions was evident in most of the top 10 active ingredient
product families examined.

2. Are the historical emission inventory data generally reliable?
Answer: "No." Several problems with the historical inventory are evident. These problems
include (but are not limited to):
- the use of metam sodium fumigant "TGA-based" EPs = 0.
- nonzero calculated emissions for inorganic pesticides such as sodium chlorate, aqueous
  bleach solutions, sulfur dioxide, carbon dioxide, liquid nitrogen, sulfuryl fluoride and
  others.
- exclusion of high-use organic pesticide products from the inventory.

These and other shortcomings in the historical inventory have been documented (Spurlock
2002a, 2002b). While recent revisions to EP estimation and VOC inventory calculation
procedures have remedied the most severe problems, further minor refinements are on-going.

REFERENCES

DPR. 1995. March 3, 1995 letter from B. Cortez, Chief, Registration Branch, to registrants. RE: Reevaluation of certain solid formulation economic poisons in order to estimate volatile organic compound (VOC) content.

Spurlock, F. 2002a. Memorandum to J. Sanders. Methodology for determining VOC emission potentials of pesticide products. January 7, 2002. Environmental Monitoring Branch, Dept. Pesticide Regulation. available on-line: <http://www.cdpr.ca.gov/docs/pur/vocproj/intro.pdf>, verified November 20, 2002.

Spurlock, F. 2002b. Procedures for estimating VOC emissions from pesticides. EH 02-03. Environmental Monitoring Branch, Dept. Pesticide Regulation. available on-line: <http://www.cdpr.ca.gov/docs/pur/pur01rep/01_pur.htm>, verified November 1, 2002.

bcc: Spurlock Surname File

Figure 1. Historical (prior to revision) and revised VOC emission estimates in San Joaquin Valley non-attanment area (NAA 2)
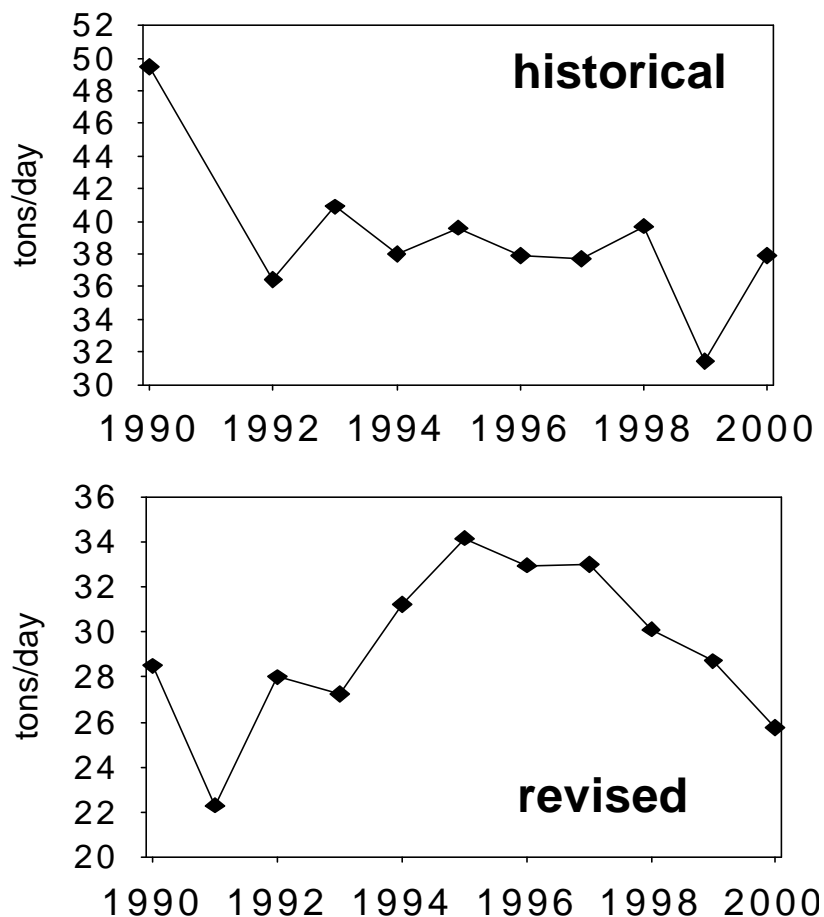
Figure 2. Mean daily pesticide use in NAA 2, 1990 - 2000
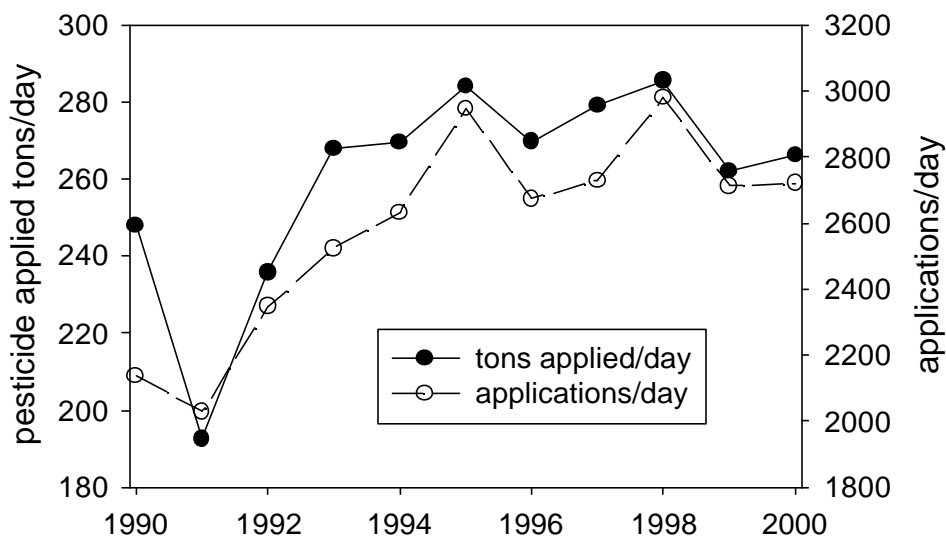
Figure 3. Emissions vs Use

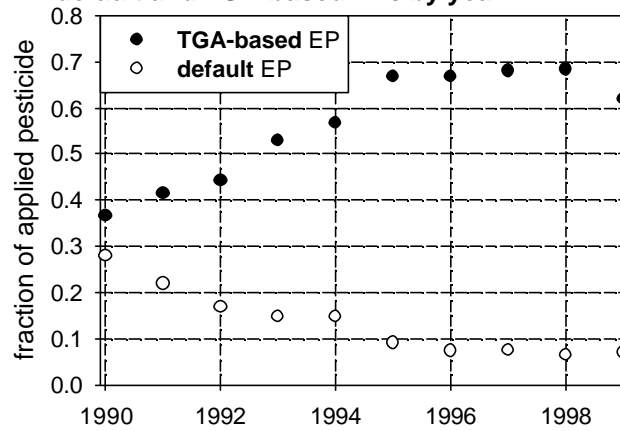revised inventory emissions vs pesticide use
1990 - 2000 annual data
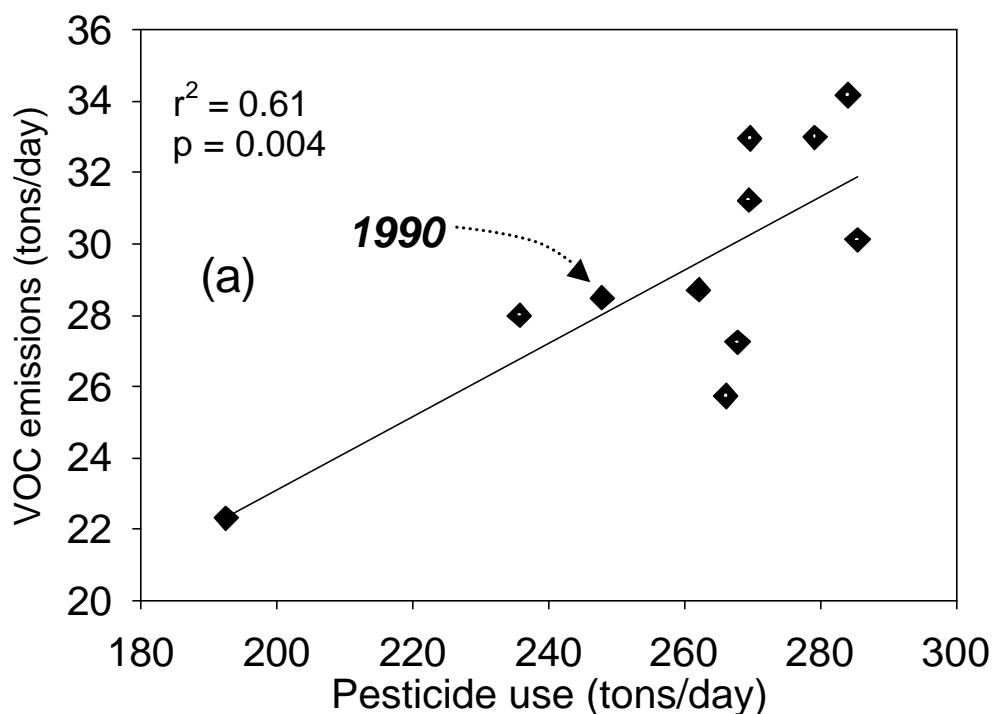
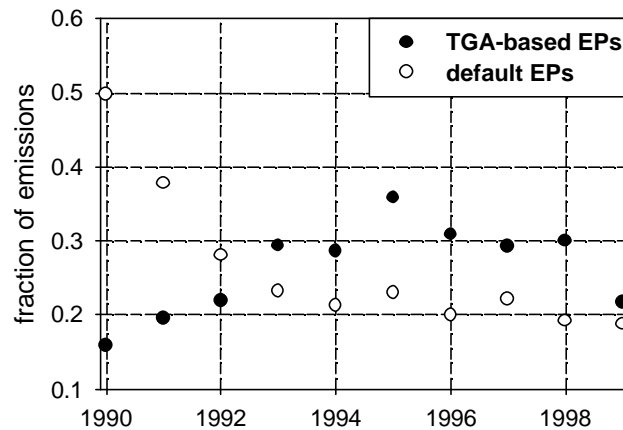historical inventory emissions vs pesticide use
1990 - 1999 annual data
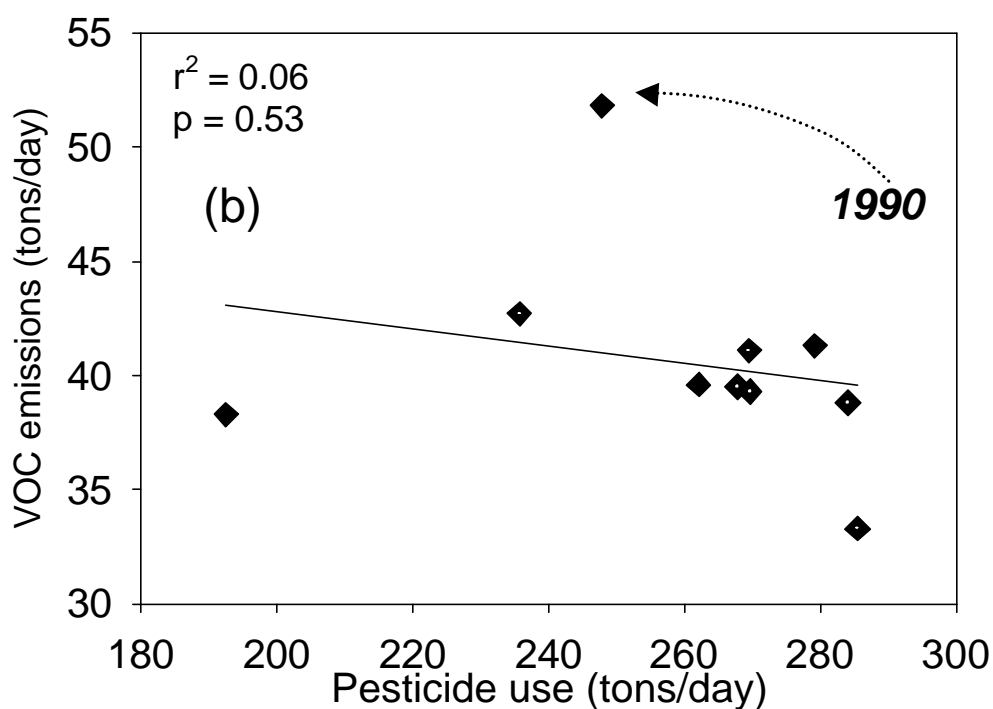
**Figure 4. Distribution of TGA EPs for Flowable Concentrate formulation products (n=46)**
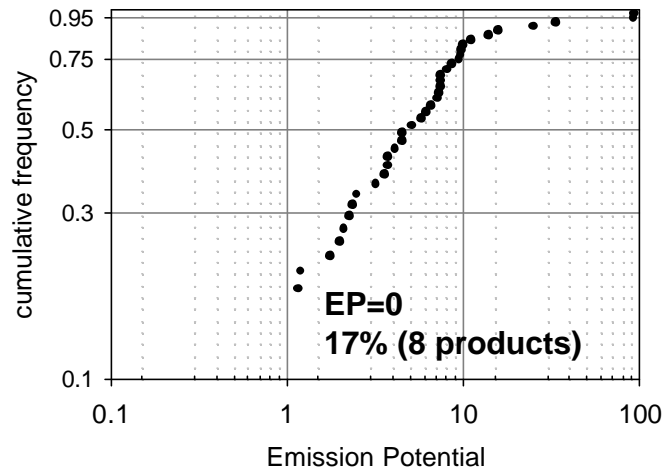
Figure 5. mass fraction of applied pesticides with default and TGA-based EPs by year in NAA 2

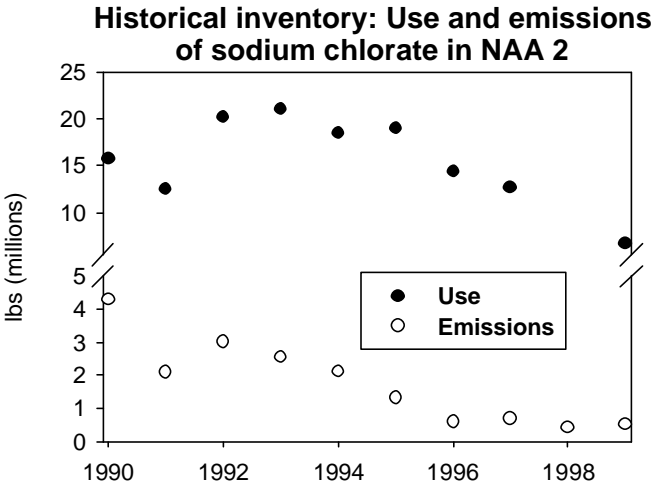**Figure 6. Historical data: mass fraction of 1990 - 1999 emissions calculated from TGA-based EPs and default EPs**

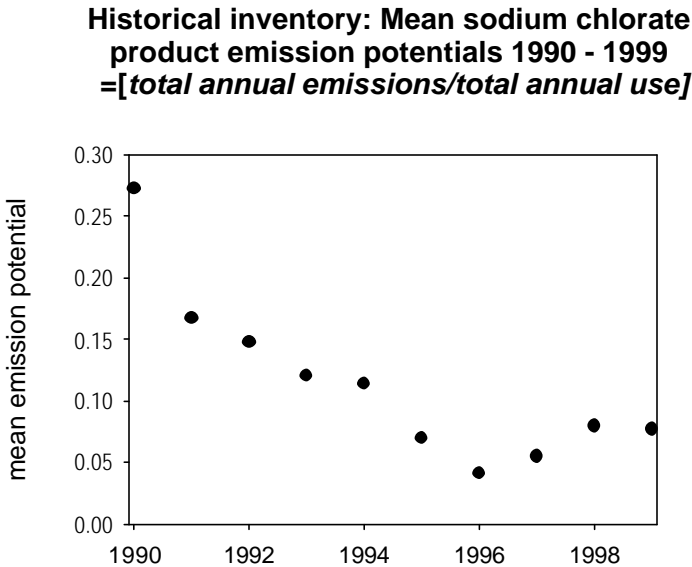# Figure 7. Fumigant use: methyl bromide and 1,3-dichloropropene in NAA 2 1990 - 2000
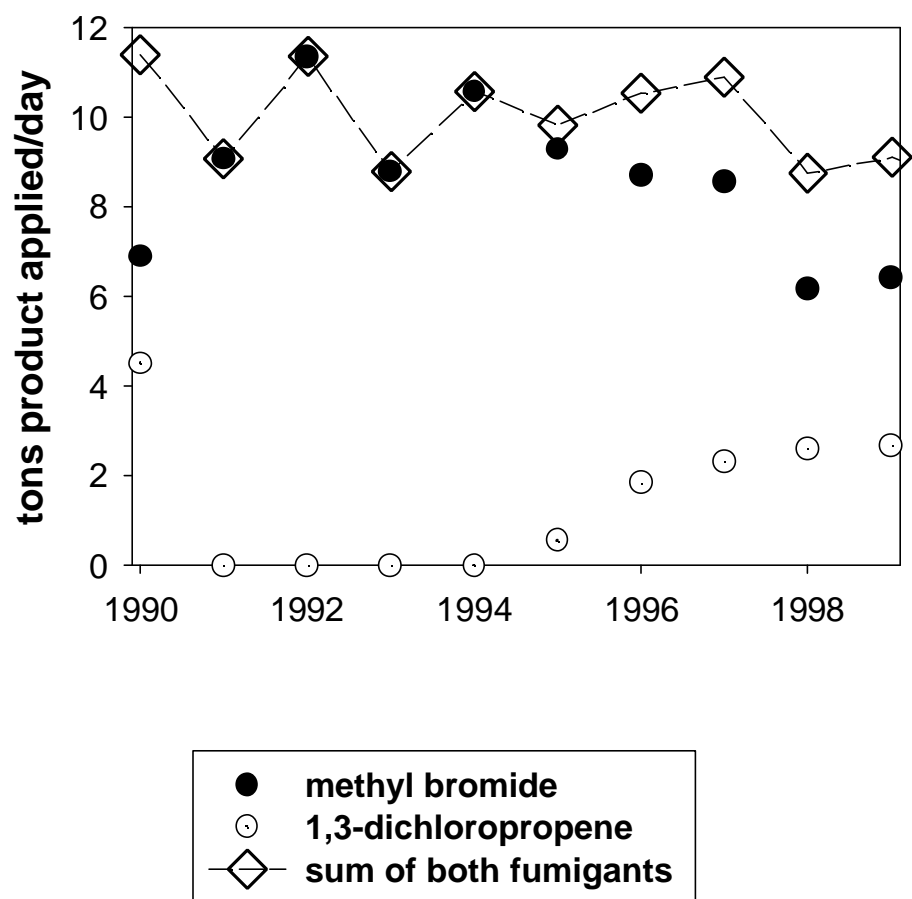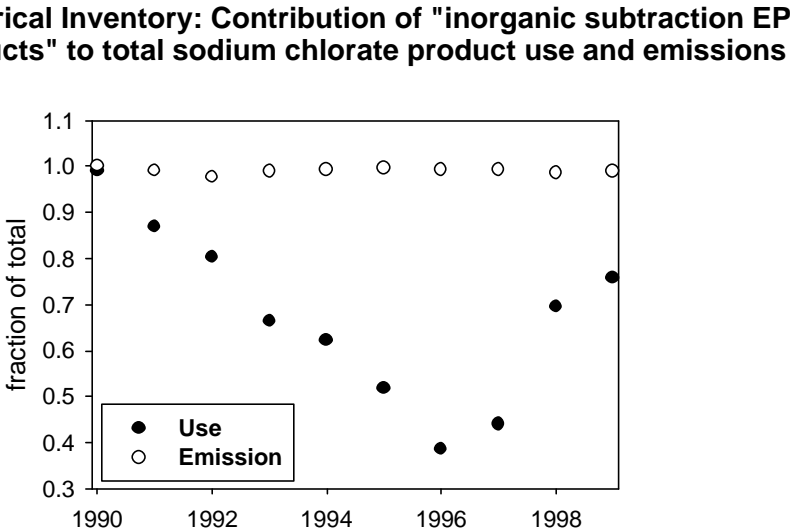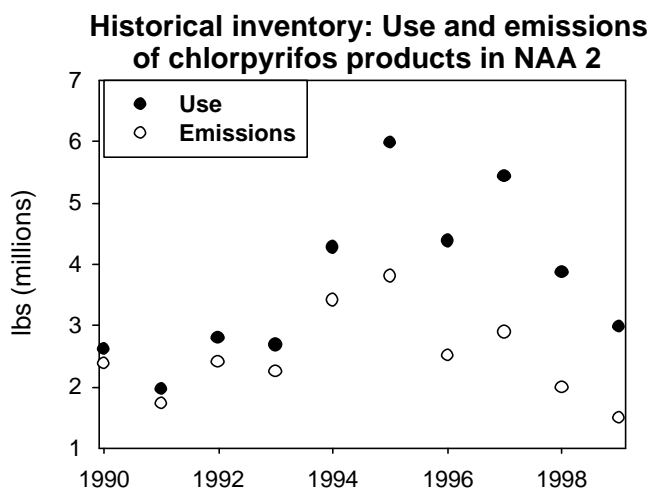
Figure 8. sodium chlorate products

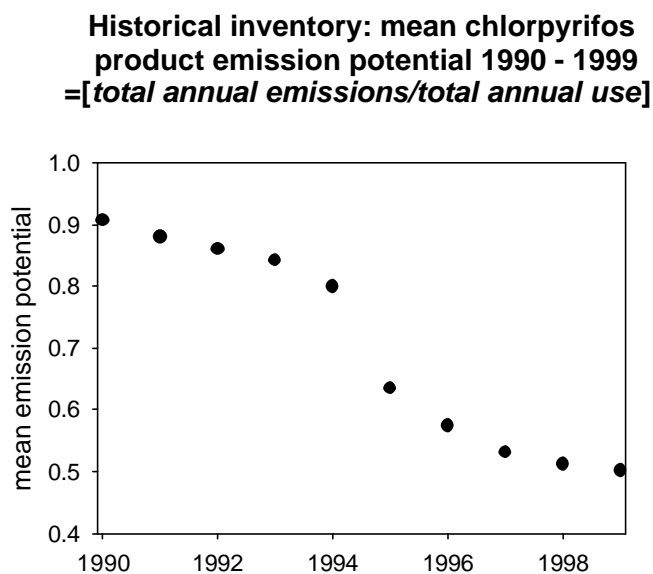**Historical inventory: Use and emissions of sodium chlorate in NAA 2**

(A)

Historical inventory: Mean sodium chlorate product emission potentials 1990 - 1999 =[*total annual emissions/total annual use]*

(B)

Historical Inventory: Contribution of "inorganic subtraction EP products" to total sodium chlorate product use and emissions

(C)

Figure 9. chlorpyrifos products

Historical inventory: Use and emissions of chlorpyrifos products in NAA 2

(A)

Historical inventory: mean chlorpyrifos product emission potential 1990 - 1999 =[*total annual emissions/total annual use*]

(B)

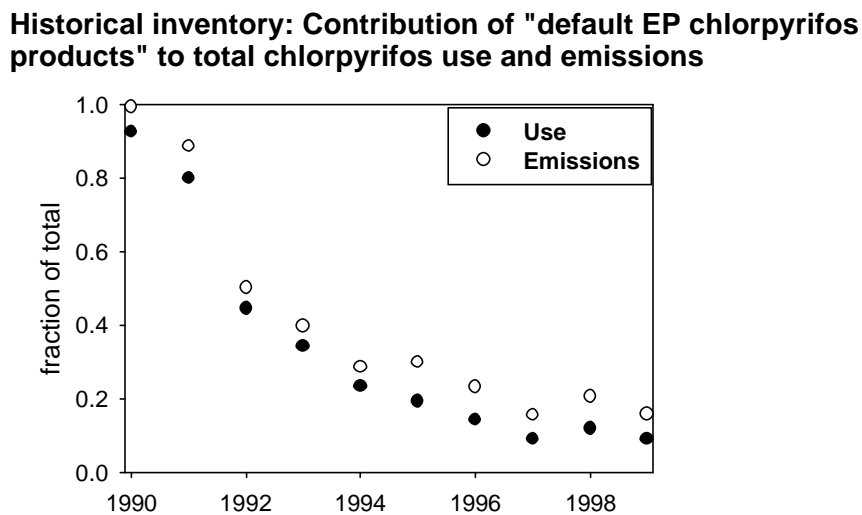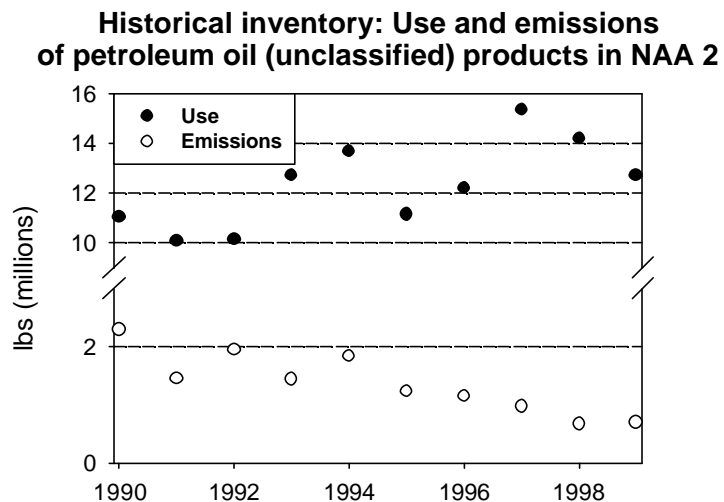**Historical inventory: Contribution of "default EP chlorpyrifos products" to total chlorpyrifos use and emissions**

(C)

Figure 10. petroleum oil (unclassified) products

Historical inventory: Use and emissions of petroleum oil (unclassified) products in NAA 2

(A)

Historical inventory: mean petroleum oil (unclassified) product emission potential 1990 - 1999 = [*total annual emissions/total annual use*]

(B)

Historical inventory: contribution of "default EP petroleum oil products" to total petroleum oil use and emissions
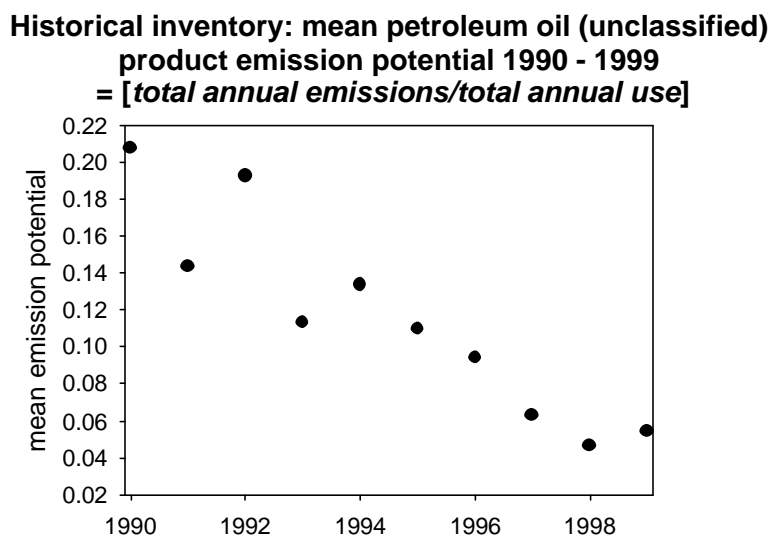
(C)
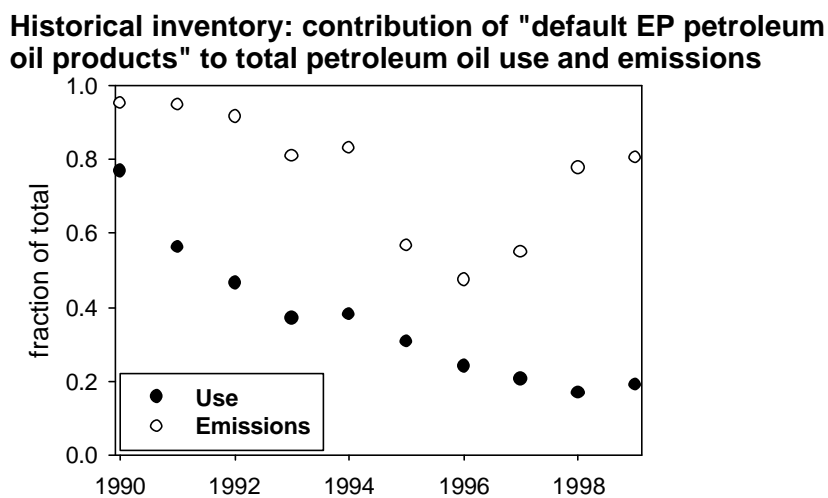
Figure 11. Metam sodium products

Historical inventory: Use and emissions of metam-sodium products in NAA 2

(A)

- Use
- Emissions

lbs (millions)

Fraction of total metam sodium product use in NAA 2 comprised of products with TGA-based EPs

(B)

fraction of total use
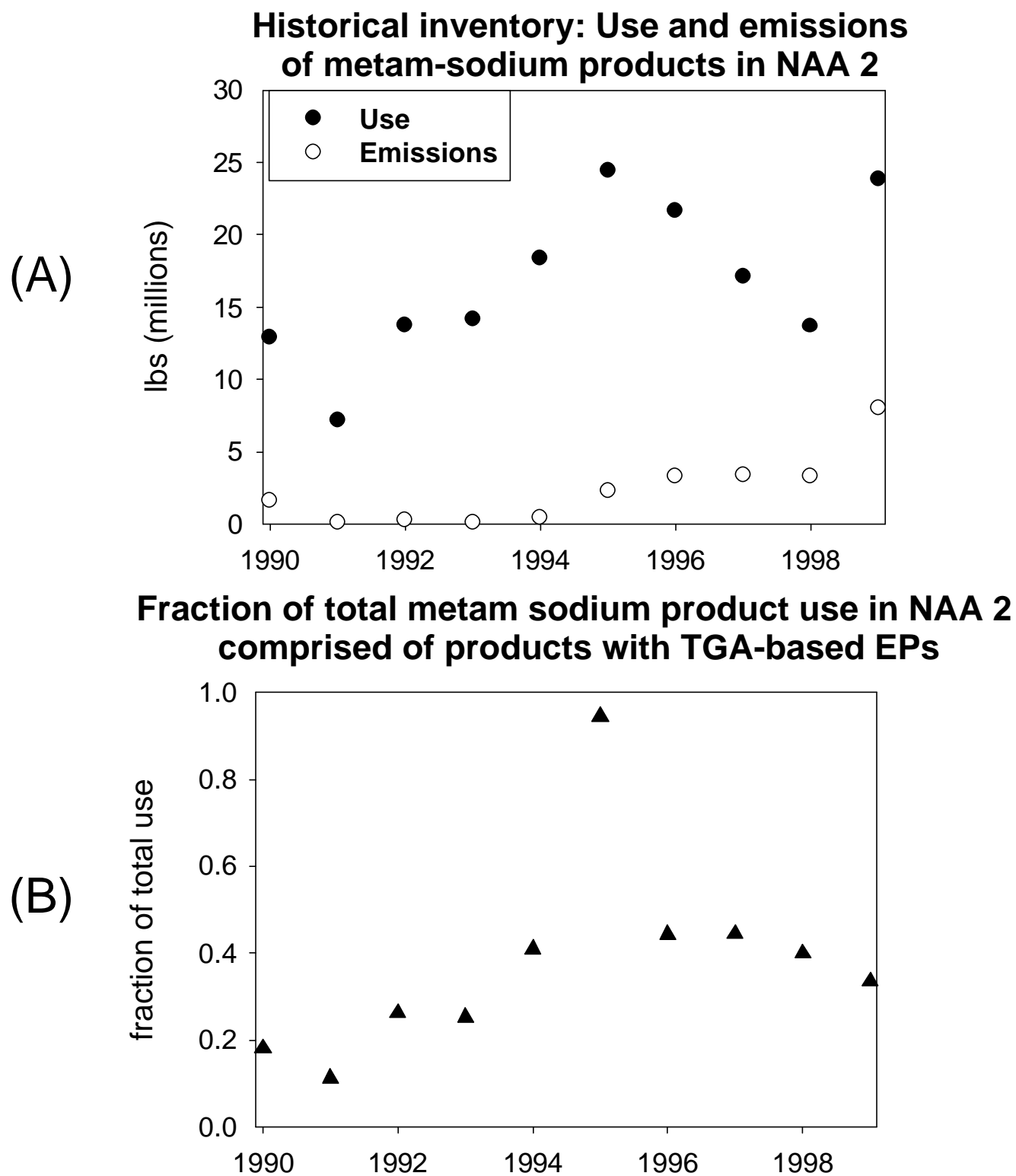
Figure 12. trifluralin products

(A)

Historical inventory: Use and emissions of trifluralin products in NAA 2

(B)

Historical inventory: mean trifluralin product emission potential 1990 - 1999 =[*total annual emissions/total annual use*]

(C)

Historical inventory: Contribution of "default EP trifluralin products" to total trifluralin use and emissions
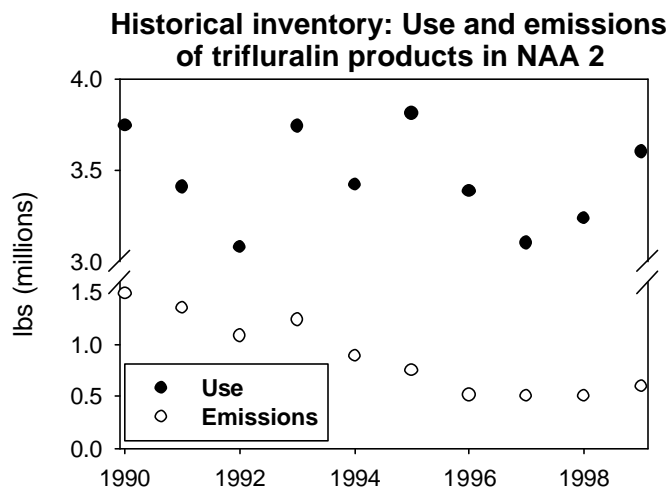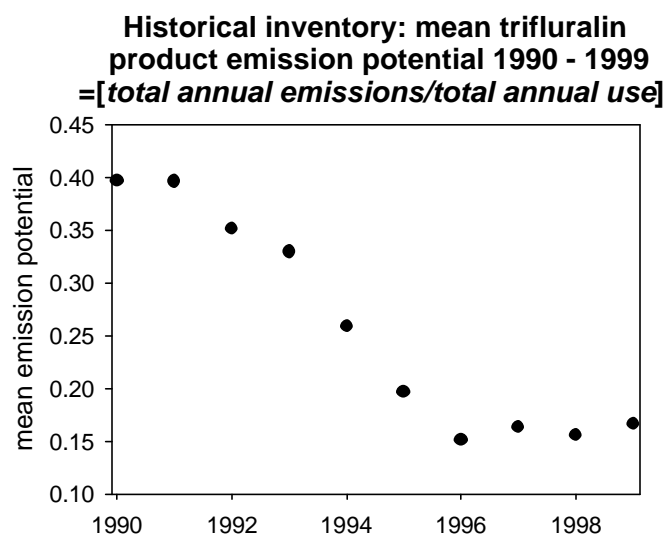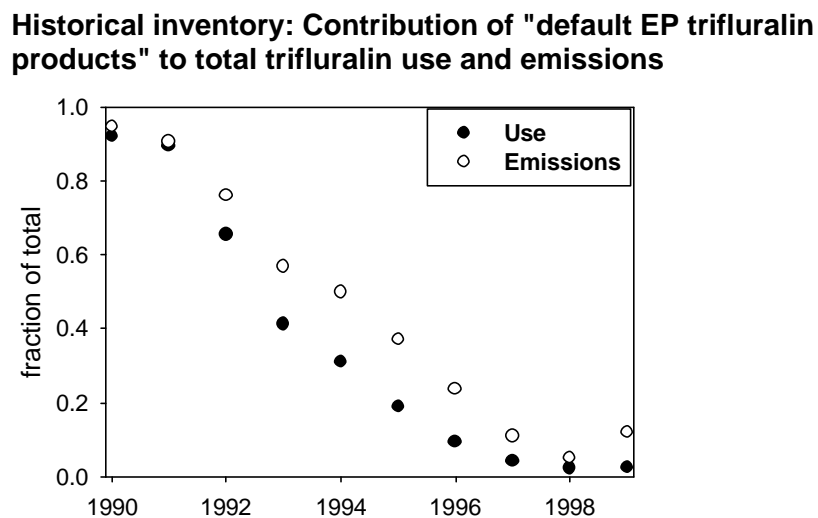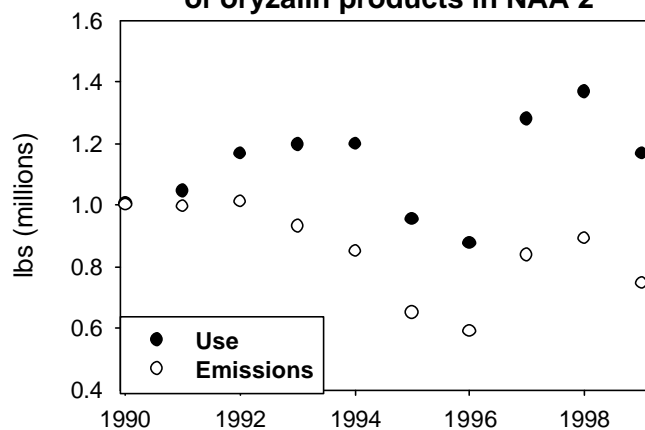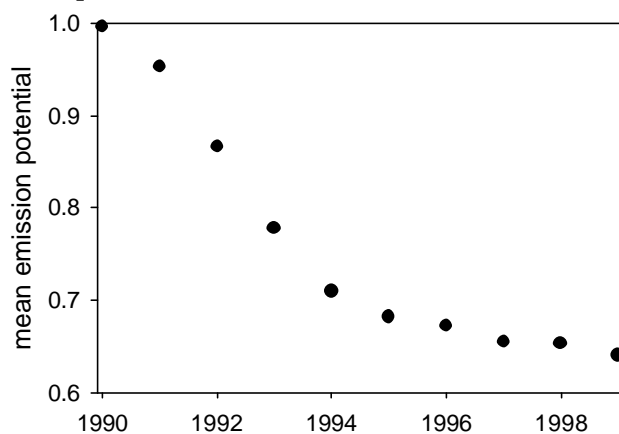
Figure 13. oryzalin products

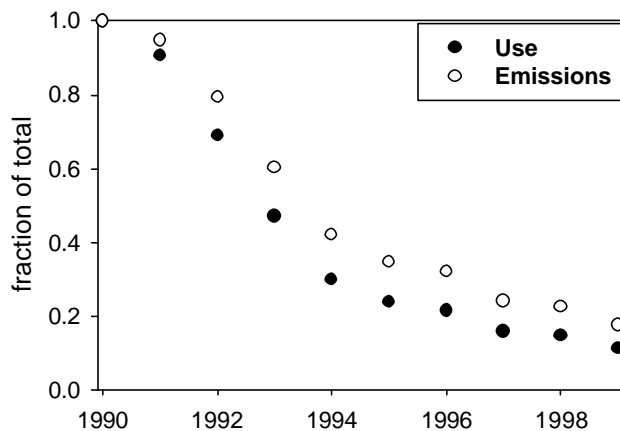**Historical inventory: Use and emissions
of oryzalin products in NAA 2**

(A)

**Historical inventory: mean oryzalin
product emission potential 1990 - 1999
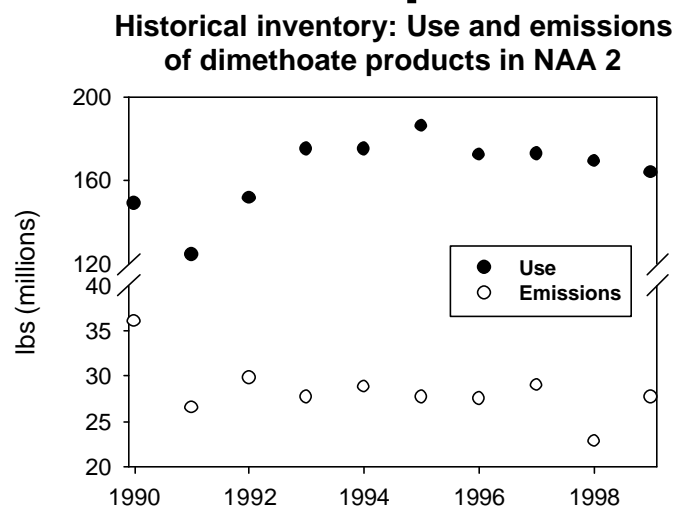=[*total annual emissions/total annual use*]**

(B)

**Historical inventory: Contribution of "default EP oryzalin
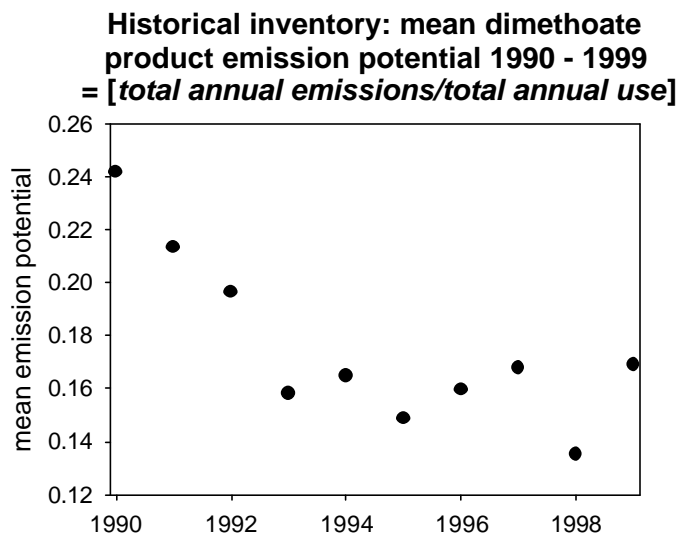products" to total oryzalin use and emissions**

(C)

Figure 14. dimethoate products

Historical inventory: Use and emissions of dimethoate products in NAA 2

(A)

Historical inventory: mean dimethoate product emission potential 1990 - 1999 = [*total annual emissions/total annual use*]

(B)

Historical inventory: contribution of "default EP dimethoate products" to total dimethoate use and emissions
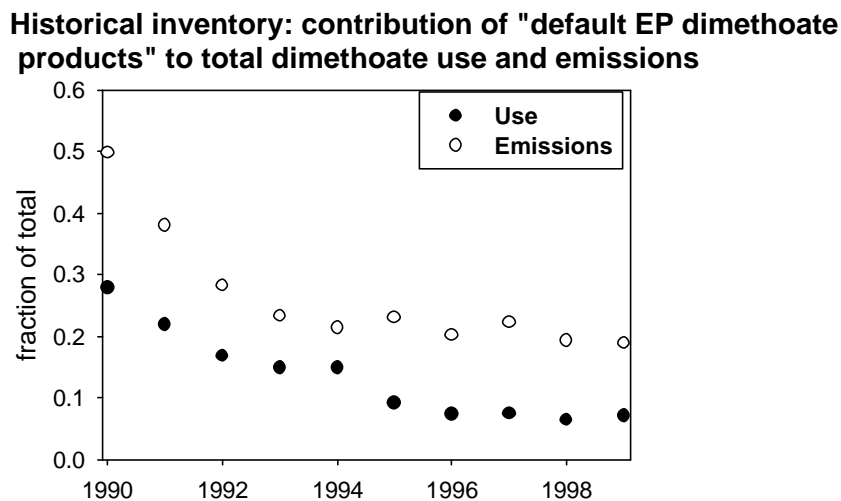
(C)

Figure 15. sulfur products

Historical inventory: Use and emissions of sulfur products in NAA 2

(A)

Historical inventory: mean sulfur product emission potential 1990 - 1999 =[*total annual emissions/total annual use*]

(B)

Historical inventory: Contribution of "default EP sulfur products" to total sulfur use and emissions

(C)